# Effect of cadmium selenide quantum dots on the dielectric and physical parameters of ferroelectric liquid crystal

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The effect of cadmium selenide quantum dots (CdSe QDs) on the dielectric relaxation and material constants of a ferroelectric liquid crystal (FLC) has been investigated. Along with the characteristic Goldstone mode, a new relaxation mode has been induced in the FLC material due to the presence of CdSe QDs. This new relaxation mode is strongly dependent on the concentration of CdSe QDs but is found to be independent of the external bias voltage and temperature. The material constants have also been modified remarkably due to the presence of CdSe QDs. The appearance of this new relaxation phenomenon has been attributed to the concentration dependent interaction between CdSe QDs and FLC molecules. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4890352]

## I. INTRODUCTION

Quantum dots (QDs) have been found very promising candidates due to their size dependent quantum confinement phenomenon. They have been extensively utilized in the application based modern research fields such as photovoltaic, optoelectronics, light emitting diodes, lasers, and drug delivery systems.[1–5] Besides their utilization in thrust areas, the research fields such as liquid crystals (LCs) have been equally benefitted in association with the QDs. The presence of the larger values of dipole moments on them may constructively couple with the molecular dipoles of the LC molecules which could modify effectively the electro-optical properties of the composites. This makes QDs suitable and potential candidates to be dispersed in LC matrix to tune the material properties of the composites.[6] The addition of nano and micro structured material in the host LC matrix causes a restructured optical, electro-optical, and alignment properties.[7,8] The formation of organized nano-composite based on CdSe QDs and H-bonded LC polymers is reported by Shandryuk *et al.*[9] Recently, the effect of doping of magic-sized CdSe QDs in the nematic LC and discotic LC has also been reported.[10,11] The introduction of ferroelectricity in LC resulted a new interesting class of LCs namely ferroelectric LCs (FLCs).[12] The properties such as faster switching, low threshold voltage, and bistability made FLCs very useful over the conventional nematic LCs.[13] The electro-optical properties of FLC materials may further be improved by mixing them with suitable QDs. Remarkable increase in the spontaneous polarization and pronounced memory effect in FLCs have been observed by doping with CdTe QDs.[14,15] The fast reorientation of the LC molecules from planar to homeotropic (HMT) orientation by introducing the CdSe/ZnS QDs in LC matrix has been observed by Shurpo *et al.*[16] In most of the studies based on QDs/FLCs composites, the main emphasis has been on the physical and electro-optical properties of the composites. However, the effect of QDs on the dielectric relaxation phenomenon of FLC materials is rarely reported. The presence of suitable amount of QDs may induce new relaxation modes other than the characteristic Goldstone and soft mode.

In the present paper, we report the effect of CdSe QDs on the dielectric relaxation phenomenon of a FLC material Felix 16/100 in detail. A new relaxation mode has been introduced in FLC material due to the presence of CdSe QDs in it. The characteristics of this new mode are found to be strongly dependent on the concentration of CdSe QDs. For 0.5 and 1.0 wt. % concentration of CdSe QDs, the observed new mode showed strong independence on the bias voltage and temperature. The relaxation frequency of this new mode is greatly varied with the QDs concentration. The preliminary communication on this CdSe QDs/FLC composite and a brief study of this new relaxation mode has recently been reported by our group.[17] It has also been observed that the presence of QDs has remarkably modified the material parameters of the FLC. The appearance and characteristics of new relaxation mode has been discussed on the basis of the concentration dependent interaction between CdSe QDs and FLC molecules.

## II. EXPERIMENTAL

A commercially available FLC material, namely Felix 16/100, is purchased from Clariant Chemicals Co. Ltd. Germany. The phase sequence of the FLC material is as follows:

$$\text{Cryst.} \overset{-20^0C}{\longrightarrow} \text{SmC}* \overset{72^0C}{\longrightarrow} \text{SmA} \overset{82^0C}{\longrightarrow} \text{N}* \overset{90\text{–}94^0C}{\longrightarrow} \text{Iso.}$$

(FELIX 16/100)

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The CdSe QDs were synthesized using the method given in Ref. 18 and characterized for their shape, size, and morphology. The size of the synthesized CdSe QDs was found to be ~3.5 nm. Conducting (~10 Ω/□) indium tin oxide (ITO) coated glass plates were used to make sample cells. The desired electrode pattern on the ITO substrates was achieved using photolithographic technique. The active electrode area was 1 $cm^2$. The uniform thickness of the FLC sample cells was maintained by means of 5 $\mu$m thick Mylar spacer. The planar alignment was obtained on polymer (Nylon 6/6) coated glass plate by unidirectional rubbing. The empty sample cells were calibrated using analytical reagent (AR) grade Carbon tetrachloride ($CCl_4$) and Benzene ($C_6H_6$). The QDs/FLC composite system was prepared by the mixing of different concentration of QDs with pure FLC 16/100. An appropriate amount (in the weight ratio) of CdSe QDs were dispersed into the pure FLC and then homogenized with an ultrasonic mixer at 90 °C for 1 h to ensure uniform dispersion of CdSe QDs. The pure and CdSe QDs dispersed FLC materials were filled in the sample cells in isotropic phase by means of capillary action and then cooled gradually to room temperature. The alignment of the samples was analyzed by the polarizing optical microscope (POM) under the crossed polarizer-analyzer arrangement. The dielectric spectroscopy of the pure and CdSe QDs dispersed FLC was performed by a computer controlled Impedance/Gain phase Analyzer (HP 4194 A) attached with a temperature controller in the frequency regime of 100 Hz-10 MHz. The dielectric measurements were carried out as a function of temperature by placing the sample on a computer controlled hot plate INSTEC (HCS 302). The temperature stability of the samples was ±0.1 °C.

## III. RESULTS AND DISCUSSION

### A. Analysis on alignment of CdSe QDs/FLC composites

The uniform dispersion of the CdSe QDs in FLC matrix has been analyzed by the POM. Figure 1 shows the optical micrographs of CdSe QDs dispersed (with different concentrations) FLC material Felix 16/100. It can be seen from the figure that the presence of QDs remarkably modified the FLC alignment. The light leakage in the dark states of 0.5 wt. % QDs dispersed FLC has been increased remarkably, which could be attributed to the tendency of QDs (low concentrations) to induce HMT alignment in LC molecules.[19,20] The competition between planer alignment (due to rubbed polyimide layer) and QDs induced HMT alignment has been resulted in the form of a dispersed type state of the FLC material. The tendency of inducing HMT alignment by CdSe QDs has clearly been reflected from inset of Figure 1(c), which shows the optical micrograph of 0.5 wt. % CdSe QDs/FLC composites in untreated glass slides. However, on increasing the concentration of CdSe QDs, the composites favored homogeneous (HMG) alignment. The minimum light leakage is observed in case of 2 wt. % CdSe QDs/FLC composite. The dual alignment (HMT and HMG) nature has clearly been reflected from the behavior of material constants of the composites, which is discussed later in the manuscript.

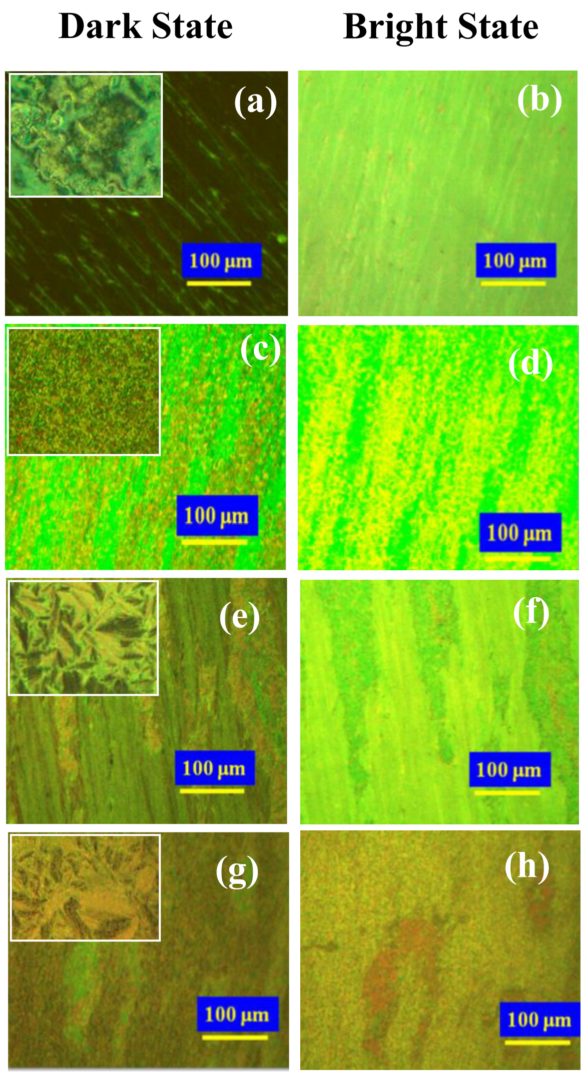


FIG. 1. Optical micrographs in unaligned (insets) and planar aligned samples of pure (a) (b), 0.5 wt. % (c) (d), 1 wt. % (e) (f), and 2 wt. % (g) (h) CdSe QDs dispersed FLC material Felix 16/100. Polarizer and analyzer have been kept in crossed orientation for all samples.

This dual alignment characteristic could be understood by taking into account some earlier reports on nanomaterials induced alignment of LC materials. In this regard, the doping concentration of nanomaterials plays an important role which governs the possible interaction between LC and nanomaterials. Qi *et al.* investigated how the alignment of a nematic LC material could be tuned by adjusting the concentration of the suspended Au NPs in it.[21,22]

### B. Dielectric relaxation studies of CdSe QDs/FLC composites

After analyzing the effect of CdSe QDs on the FLC alignment, we studied the dielectric relaxation phenomenon of QDs/FLC composites. Figure 2 shows the behavior of dielectric loss factor (tan $\delta$) of pure and CdSe QDs dispersed FLC 16/100 material at room temperature. The occurrence of characteristic Goldstone mode in pure and CdSe QDs dispersed FLC material can be clearly seen from the figure. However, the magnitudes of tan $\delta$ and relaxation frequency (corresponding to tan $\delta$ maximum) have been changed in

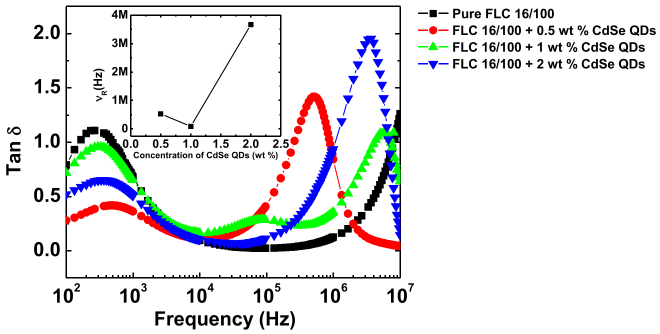


FIG. 2. Behavior of room temperature dielectric loss factor (Tan $\delta$) of pure and CdSe QDs dispersed FLC material Felix 16/100 with frequency. The inset of the figure shows the variation of relaxation frequency (corresponding to tan $\delta$ maximum) with concentration of CdSe QDs.

case of QDs dispersed FLC samples. The value of tan $\delta$ gets reduced remarkably, and the relaxation frequency is increased for QDs dispersed samples in comparison to pure FLC. It is worth to mention here that the presence of CdSe QDs have induced a new relaxation mode in addition to the characteristic Goldstone mode [Figure 2]. As clearly visible from Figure 2, the appearance of this new relaxation mode strongly depends on the doping concentration of QDs. The relaxation frequency of the new mode has greatly been varied with the concentration of QDs. To analyze further characteristics, we observed the temperature and bias dependence of this new mode. Figure 3 shows the behavior of tan $\delta$ of CdSe QDs dispersed FLC samples with temperature at 0 V. The new relaxation mode is found to be quite independent of the temperature of the samples for all concentrations of QDs. The relaxation frequency and tan $\delta$ values have hardly been changed on changing the temperature. Interestingly, the relaxation mode remained pronounced even beyond the Sm C*-Sm A phase transition temperature. However, the dielectric relaxation corresponding to the new mode has been appeared in the frequency range over which the relaxation due to ITO appears in case of 2 wt. % QDs concentration. Therefore, it is difficult to assign this relaxation as a new mode and we may conclude that the new relaxation mode get disappeared or merged with the characteristic ITO relaxation in case of higher concentration (2 wt. %) of CdSe QDs.

Figure 4 shows the effect of bias voltage on the behavior of new relaxation mode. The suppression of characteristic GM by the application of bias voltage has clearly been observed for 1 and 2 wt. % QDs dispersed FLC [Figures 4(c) and 4(d)]. However, surprisingly the GM exhibited bias independence and could not be suppressed even at higher bias voltages in case of 0.5 wt. % QDs concentration [Figure 4(b)]. The critical field to unwind the helical structure is found to be 9 V, 12 V, and 7 V for the pure, 1 wt. % and 2 wt.% CdSe QDs dispersed FLC, respectively. This observation shows that the helical structure of the Felix 16/100 molecules dispersed with 1% QDs is more stable than that of the pure Felix 16/100 whereas for 2% QDs dispersed Felix 16/100, it is less stable as compared with pure Felix 16/100. The significant modification in the relaxation phenomenon has been observed only in case of 0.5 and 1 wt.% CdSe QDs dispersed FLC material where the appearance of new relaxation mode is pronounced. As far as range of relaxation frequency in concerned, the new relaxation mode seems to have resemblance with the characteristic soft mode relaxation in FLC materials, which arises due to tilt fluctuations.[23] It is worth to be mentioned here that the soft

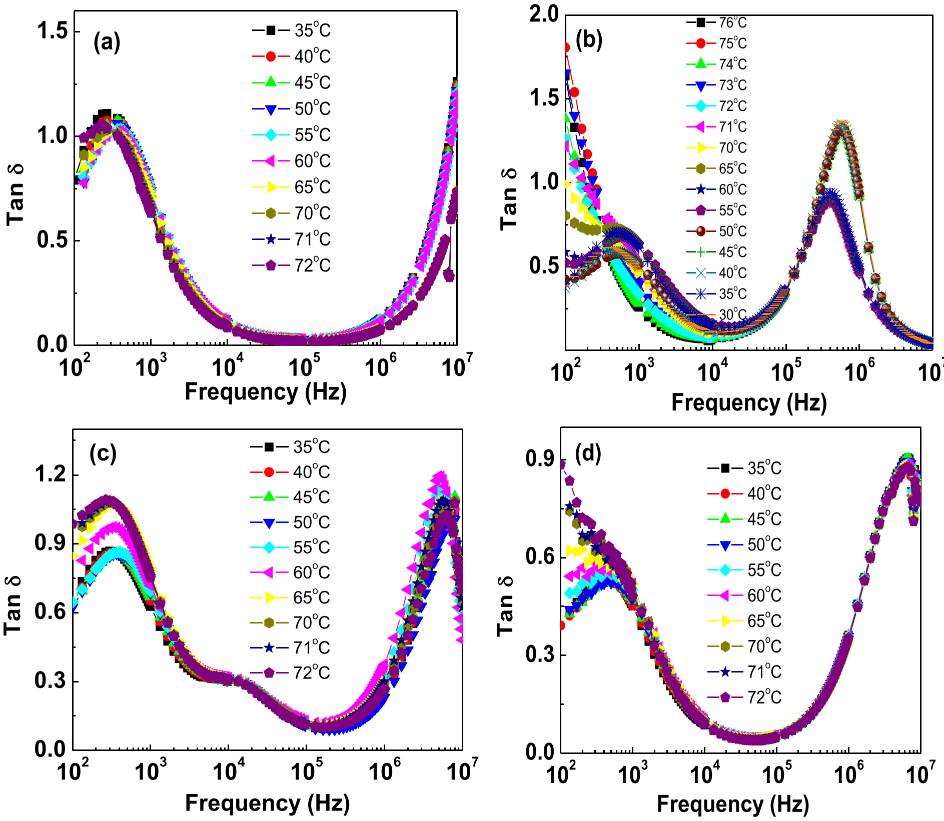


FIG. 3. Behavior of dielectric loss factor (Tan $\delta$) of pure (a), 0.5 wt. %, (b) 1 wt. %, (c) and 2 wt. % (d) CdSe QDs dispersed FLC material Felix 16/100 with frequency at different temperatures.

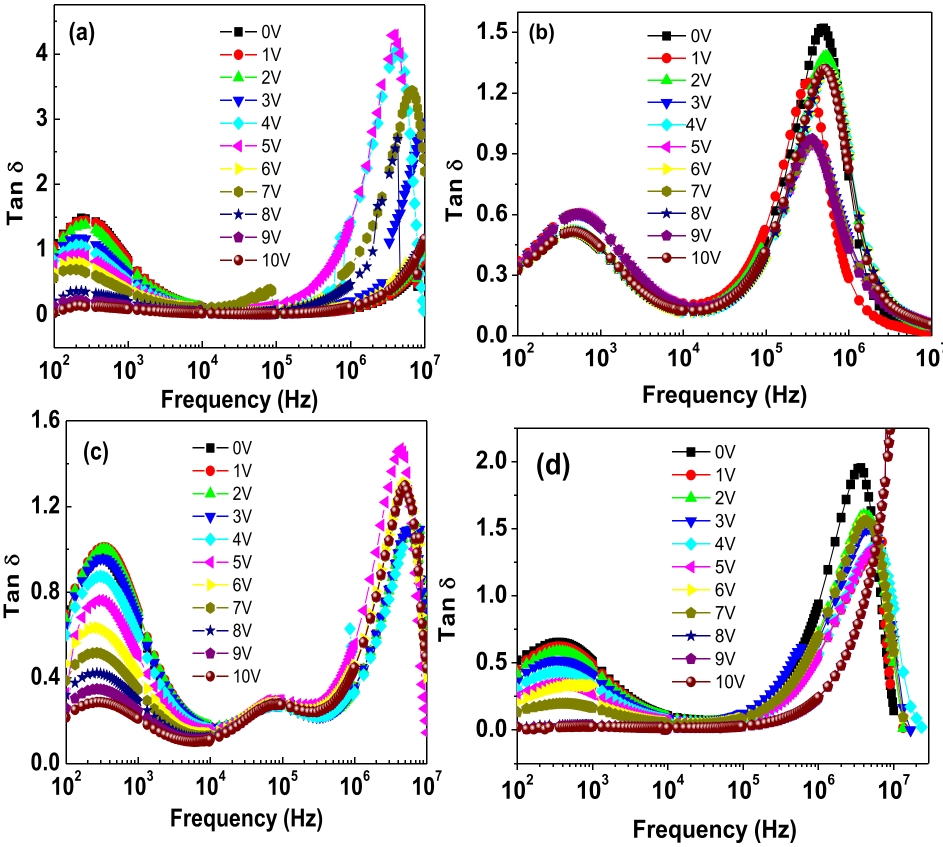


FIG. 4. Room temperature behavior of dielectric loss factor (Tan $\delta$) of pure (a), 0.5 wt. %, (b) 1 wt. %, (c) and 2 wt.% (d) CdSe QDs dispersed FLC material Felix 16/100 with frequency at different dc biases.

mode is not visible in case of pure FLC Felix 16/100 material. The large values of dipole moment of CdSe QDs may enhance the tilt fluctuations in the FLC material and at first sight, the new relaxation mode may be assigned as soft mode which get envisaged due to the presence of CdSe QDs. However, the properties of this induced new mode are found to be different than that of the characteristic soft mode exhibited by FLC materials. In fact, the characteristic soft mode is visible only very near to the SmC*- SmA* phase transition and its relaxation frequency increases very sharply with temperature. The induced relaxation mode observed in case of CdSe QDs dispersed FLC is almost independent of temperature and more significantly, it appeared profoundly at room temperature along with the GM. Second, this new mode showed bias independent nature and suppression of GM is not observed (in case of 0.5 wt. % CdSe QDs) even after applying enough bias voltage. The existence of new relaxation mode in the CdSe QDs/FLC composite is peculiar, which varies with the dopant concentration. It is believed that new relaxation mode exists in all CdSe QDs/FLC composites but no separate relaxation peak was observed except in the 1 wt. % Cdse QDs dispersed FLC system. The careful analysis of bias study suggests that the new relaxation mode implicit with the GM in the 0.5 wt. % CdSe QDs dispersed FLC; whereas for 1 wt. % CdSe QDs dispersed FLC, it is shifted towards higher frequency side and clearly appears near $10^5$ Hz. Again on increasing the QDs concentration (2 wt. %) in the FLC, new relaxation merges with the ITO relaxation. GM do not suppress even at 10 V for 0.5 wt. % QD/FLC composite, which suggests that the new relaxation mode debars the suppression of GM with the application of bias voltage. The bias study of CdSe QDs/FLC composite implies the addition of QDs induce new relaxation mode which strongly depends upon the dopant concentration and shift towards higher frequency side with the increase in CdSe QDs concentration. The introduction of the new relaxation phenomenon in FLC material could be attributed to the concentration dependent interaction between FLC material and CdSe QDs. The high frequency relaxation phenomenon in pure and 2 wt. % CdSe QDs dispersed FLC samples has been occurred in the frequency range where relaxation due to ITO appears; therefore, they can be attributed due to ITO itself. For relaxation processes (other than GM) observed in case of 0.5 and 1 wt. % CdSe QDs dispersed FLC material could have some different origin. The CdSe QDs possess larger values of dipole moments and the dipolar relaxation in a good quality dispersion of these QDs may appear in the form of a broad relaxation peak around $10^5$ Hz.[24] In our case, the relaxation frequencies of the new relaxation mode have been observed in the same frequency range, which is observed for CdSe QDs in some suitable solvent. The interaction of CdSe QDs with FLC material in case of 0.5 and 1 wt. % concentrations has taken place in such a manner that both the dipolar relaxations (of FLC molecules and QDs) have profoundly occurred together. Moreover, the occurrence of the dipolar relaxation of CdSe QDs dispersed in FLC material is almost independent of external bias and temperature. It remained pronounced even in the Sm A* phase where GM is disappeared completely. The bias and temperature independent nature of this new relaxation mode due to CdSe QDs is very interesting and hence deserves further scope to be seriously investigated.

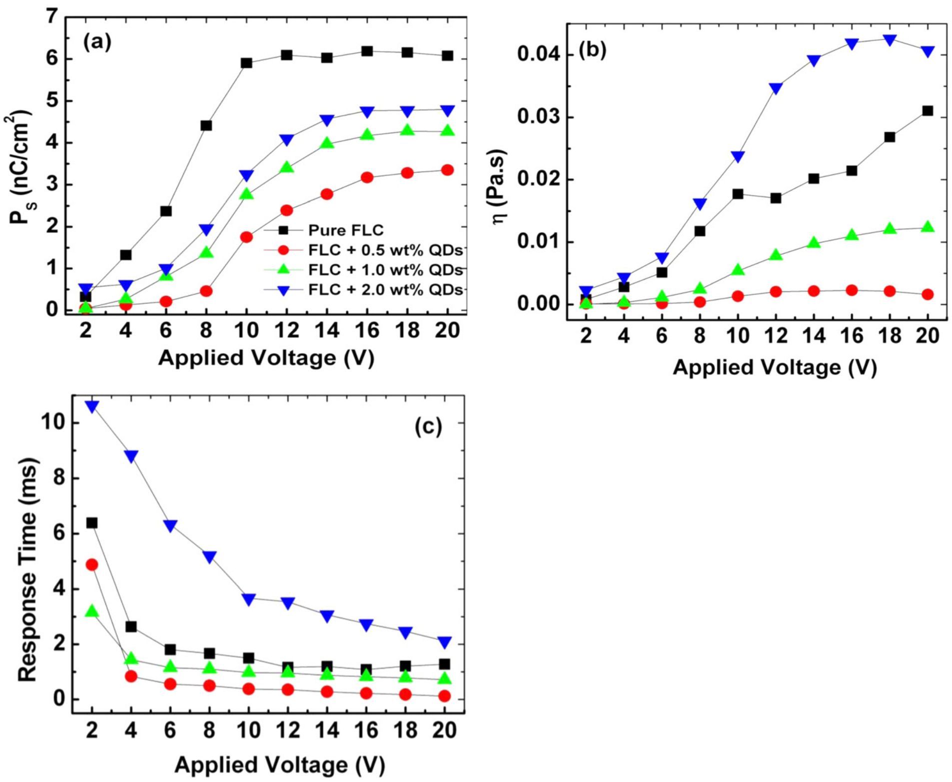


FIG. 5. Room temperature behavior of (a) spontaneous polarization (Ps), (b) rotational viscosity ($\eta$), and (c) response time of pure and CdSe QDs dispersed FLC material with applied dc bias.

### C. Material parameters of CdSe QDs/FLC composites

The presence of CdSe QDs has not only induced the new dielectric relaxation phenomenon but, at the same time, they modified remarkably the material parameters of the FLC [Figure 5]. The spontaneous polarization (Ps) of FLC material is decreased remarkably for composites with lower concentration (0.5 wt. %) of CdSe QDs. This lowering in the Ps value could be attributed to the favorable HMT alignment of FLC material in the presence of 0.5 wt. % CdSe QDs. A remarkable number of FLC molecules, being in HMT configuration, have not contributed to the Ps on application of bias voltage and the result is the lower values of Ps. On the other hand, the Ps value is increased when the doping concentration of CdSe QDs was increased beyond 0.5 wt. % due to the favorable planer alignment of the FLC molecules [Figure 5(a)]. Though an earlier study on QDs/FLC composites reported the significant increase in the Ps values for lower concentrations of the CdTe QDs due to the effective coupling between dipole moments of QDs and that of FLC molecules,[15] we observed here a decrease in Ps value. The behavior of rotational viscosity ($\eta$) followed the same trend as that of Ps for CdSe QDs/FLC composites [Figure 5(b)]. It is decreased remarkably in case of 0.5 wt % CdSe QDs concentration and gets increased further with the concentration of QDs. The value of $\eta$ is increased greatly (become greater than that of pure FLC) for sample with 2 wt. % CdSe QDs concentration. The Ps and $\eta$ values were used to determine the response time ($\tau_R$) of the composites using formula

$$\tau_R = \frac{\eta}{P_S * E}, \tag{1}$$

where E is applied electric field across the sample cells.

The value of $\tau_R$ is lowered in case of FLC samples doped with 0.5 and 1 wt. % CdSe QDs [Figure 5(c)].

## IV. CONCLUSIONS

We presented the effect of CdSe QDs on the dielectric properties of a FLC material. Significant modification in the dielectric relaxation phenomenon caused by CdSe QDs of FLC material has been observed. A new relaxation mode is observed in CdSe QDs dispersed FLC samples, which is found to be strongly dependent on the doping concentration of CdSe QDs. Moreover, the induced mode showed almost bias and temperature independence in its dielectric behaviour. The appearance of this new relaxation phenomenon is attributed to the concentration dependent interaction between CdSe QDs and FLC molecules.

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